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The role of the network structure in determining the dielectric constant of binary and ternary oxide insulators is outlined. Seemingly anomalous behavior observed in rare-earth sesquioxides, Ta_2O_5-Ti_2 mixed oxides, lanthanum aluminate and dilute $Zr_xSi_yO_2$ is discussed in terms of the atomic structure. Physical examination of the relevant properties of these materials should lead to an understanding of how to engineer the dielectric constant.

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ON THE IMPORTANCE OF ATOMIC PACKING IN DETERMINING DIELECTRIC PERMITTIVITIES

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Abstract. The role of the network structure in determining the dielectric constant of binary and ternary oxide insulators is outlined. Seemingly anomalous behavior observed in rare-earth sesquioxides, Ta_2O_5-TiO_2 mixed oxides, lanthanum aluminate and dilute $Zr_xSi_yO_2$ is discussed in terms of the atomic structure. Physical examination of the relevant properties of these materials should lead to an understanding of how to engineer the dielectric constant.

1. Introduction

Despite a growing volume of experimental research designed to find dielectrics capable of addressing the requirements set down in the Semiconductor Industries roadmap[1] there is still no medium to long term solution for the gate oxide in metal-oxide-semiconductor field effect transistor (MOSFET) devices. Solutions may exist or the requirements may be relaxed for applications involving embedded capacitors and dynamic random access memory (DRAM) cells. For example, reactivity between the dielectric and the Si substrate will not be of concern as it is for the MOSFET where the insulator is in direct

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contact with the active semiconductor surface. Furthermore, appropriate metal gate electrodes may be chosen so as to minimize charge injection resulting from the insulator conduction band-metal conduction band barrier height and band offset[2].

Solutions for the MOSFET gate insulator have been primarily looked for beginning with simple binary oxides (M_xO_y), examples of these include[3-7] Ta_2O_5, RE_2O_3 (where RE implies a rare-earth ion), Al_2O_3, and ZrO_2 or HfO_2. These materials are beset with a variety of problems, however, such as hygroscopy, low Si conduction band-insulator-conduction band barrier height, low temperature recrystallization and subsequent grain boundary related leakage current or surface roughness issues, inadequate dielectric constant, etc., etc. A natural extension has been to begin to explore ternary compounds[8] such as $LaAlO_3$ whose nominal dielectric constant in the crystalline state is ~ 28. Again, there is evidence that in the amorphous phase which is desired for technological applications in order to avoid grain boundary effects, dielectric constants are generally < 20 and the material is subject to reaction[9] with Si when heated at elevated temperatures (for example, > 800°C).

It turns out that situations such as that for $LaAlO_3$ are not uncommon and that frequently the dielectric constant obtained in the amorphous phase of a material is significantly lower than that in the crystalline phase. Surprisingly, examples also exist, as we shall discuss, where substantially larger dielectric constants than expected may be obtained, both in amorphous and crystalline phases . We are naturally lead to ask the question why this comes about so that we might develop an understanding enabling us to design or engineer the material with the desired dielectric properties. Combining all this information leads us logically to the conclusion that time has perhaps come to endeavor to establish a deeper understanding of the relationship between the insulator dielectric constant and the atomic structure of the network of the insulator.

2.   Basics of the dielectric constant

Before treating the specific case of binary or ternary oxides we introduce the underlying physical basis which will be used throughout our discussion of existing experimental results.   Following the classical Clausius-Mossotti approach[10] for the dielectric constant, k, in terms of the molecular polarizability, α, and the molecular volume, V_m:

$$(k - 1)/(k + 2) = (4\pi/3)\,\alpha/V_m \tag{1}$$

The polarizabilities have been tabulated by various authors[11,12]. If one extends the theory to more complicated molecules one can, to first order, develop an

approximate formula based upon a linear sum of the constituent "sub-molecules":

$$(k - 1)/(k + 2) = (4\pi/3) (c_1\alpha_1 + c_2\alpha_2)/V_m \qquad (2)$$

where we assume a complex molecule $M_xL_yO_{p\text{-}q}$ can be written as a sum of the component parts M_xO_p and L_yO_q with the concentrations, c_1 and c_2, as the weighting factors. Note that this heterogeneous model assumes the insulator is comprised of independent molecules so that the relevant polarizabilities are those related to the M-O and L-O bonds generally embedded in M-O-M and L-O-Lbridges. This model does not make allowance for those bridging bonds which interlink such as M-O-L. The model appears to work, however, for a surprisingly large number of complex materials[12].
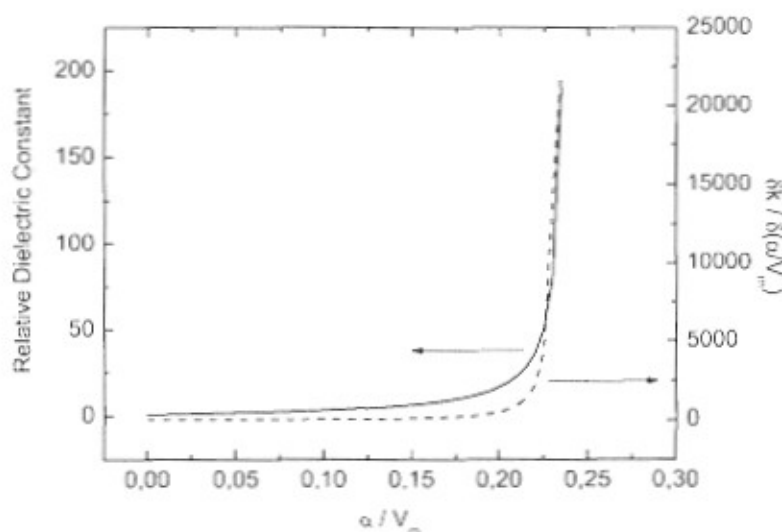

Figure 1. Variation of the relative dielectric constant, k, with α/V_m (solid line) and its derivative (dashed line) as calculated from Eq.(3)

Whether one considers Eq.(1) or Eq.(2), it is clear that the important parameter determining k is α/V_m and this underlines the importance of V_m i.e. the molecular volume or network structure. We can re-write Eq.(1) in a form which demonstrates the importance of α/V_m more rigorously:

$$k = [1 + (8\pi/3)\ \alpha/V_m]/[1 - (4\pi/3))\ \alpha/V_m] \qquad (3)$$

In Fig. 1 we represent Eq.(3) graphically (solid line) and we include its derivative (dashed line) to show how rapidly k varies with α/V_m once the value of 0.2 is exceeded. The importance of network volume, V_m, which is inversely proportional to the network density, is clearly demonstrated in Fig. 1. One sees that, if the network volume decreases (the material density increases) then k will increase providing, of course, that any variation is not compensated by a variation in α.

The polarizability term, α, is complicated because, for the low frequency dielectric constant case, it is composed of an electronic term and a term related to vibrational properties of the network[13]. Only the electronic term is relevant for optical properties (for example, the refractive index) because the vibrational part cannot follow the associated high frequency fields. This can be written:

$$\alpha_{el} = 2 \sum [(0|e \sum x_i |j)(j|e \sum x_i |0)]/(W_j - W_0) \qquad (4)$$

where the sums run over all electrons (defined by i) and all states defined by j. To a first approximation the vibrational part of the polarizability, α_{ion}, for a diatomic chain can be written:

$$\alpha_{ion} = e^2/(\mu_c V_m \omega_o^2) \qquad (5)$$

where μ_c is the reduced mass and ω_o is a characteristic vibrational frequency of the chain. In Eq.(4), the denominator is essentially the insulator bandgap and this should decrease with the molecular volume or increasing density. This would lead to a decrease in polarizability with decreasing density. From Eq.(5) the vibrational part of the polarizability should also decrease when the density decreases so that both polarizability contributions are expected to decrease as the network density decreases. It turns out[13] that for at least two systems studied practically, SiO_2 and TiO_2, the opposite happens and in fact the polarizability increases as the density decreases. This means that other volume dependent factors in Eq.(4) and Eq.(5) have been neglected. At the present time we cannot simply predict the variation of α with density and we are forced to rely upon experimental determination. Fortunately, if the SiO_2 and TiO_2 data can be used as a guide, it would appear that the influence of volume reduction with increasing density outweighs any compensating effect due to α so that k increases (Eq.(3)) as V_m decreases.

The general conclusion of this section is that the dielectric constant increases as the network volume decreases. We are now equipped to research materials where important manifestations of this effect are apparent.

3. EXAMPLES OF REAL SYSTEMS

3.1.   DILUTE AMORPHOUS SYSTEMS

The "dilute" alloy system which raised the most amount of interest and remains related to the probable choice for short term industrial development is based upon dilution of Zr in SiO_2. In fact, industrially, Hf in SiO_2 is the likely choice. However, whereas SiO_2 has a low frequency dielectric constant of 3.9, ZrO_2 has a crystalline phase constant ~ 26. The dielectric constant for the stoichiometric compound $ZrSiO_2$ is quoted as[14] 12 but the variation between pure SiO_2 and the stoichiometric compound is found to be supra-linear[14,15] and a dielectric constant of 11 is obtained for the mixed oxide $Zr_{0.15}Si_{0.85}O_2$. The dielectric constant is thus enhanced since a linearly extrapolated value for this concentration should have been ~ 6. The origin of this enhancement has been much discussed but it turns out that the most probable cause is the network structure[16].

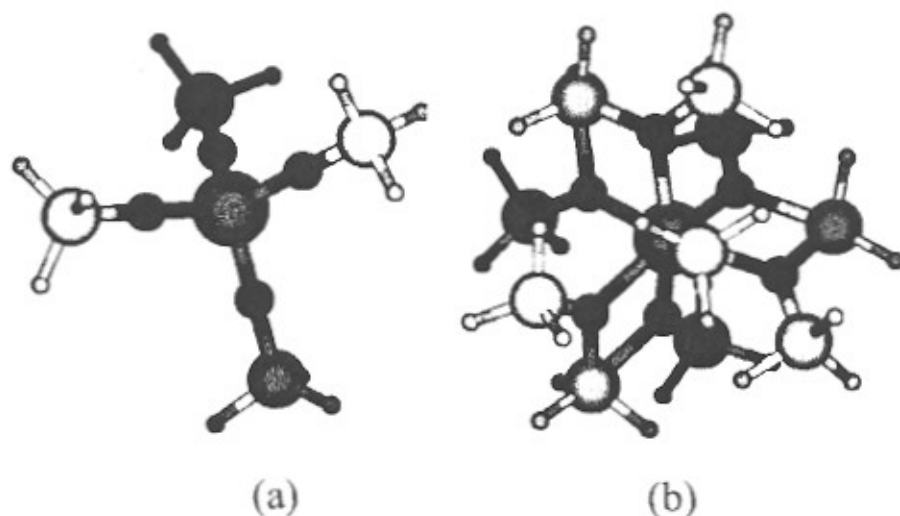(a)   (b)

Figure 2. Atomic models used in calculations (reference 16) for Zr in SiO_2. (a) Four fold coordinated Zr   (b) Seven fold coordinated Zr.   The latter is the most likely in dilute concentrations of Zr.

Initial arguments suggested that Zr simply replaced Si in the SiO_2 network and that the O coordination around the Zr was 4. However, detailed X ray absorption fine structure measurements[17] provide evidence that in dilute mixtures of ZrO_2 and SiO_2, the coordination of the Zr ion is > 7. The consequences of this enhanced coordination were explored theoretically[16] and the nature of the problem resolved. In Fig.(2) we show atomic models of the 4 fold and 7 fold coordinated structures. One striking result is that when one examines the density of the network, one clearly sees that higher coordination numbers lead to much denser networks. The effective molecular volume thus decreases leading to this higher density. The effect on the dielectric constant can be easily anticipated from the arguments relating k to molar volume presented previously. For the moment the densification resulting from higher coordination in the mixed Zr_xSi_yO2 oxide has not been quantified but the atomic structures shown in Fig.(2) leave little doubt that this is indeed the explanation for k enhancement. In support of this it is further interesting to examine density/coordination relationships for known structures. Restricting ourselves to polymorphs of ZrO_2, we show in Fig.(3) a plot of molecular volume as a function of Zr coordination using data taken from reference 18. Though there is clearly a dispersion of results, one cannot avoid the general conclusion that as the coordination increases, the molecular volume decreases leading to higher density structures.

To our knowledge there are no other examples of "dilute" systems where the dielectric constant has been measured as a function of concentration so we proceed to examine the dielectric behavior of stoichiometric, concentrated mixtures or pure materials and how this is influenced by the internal structure.

3.2.   CONCENTRATED SYSTEMS

The role of the network structure in determining the dielectric constant in concentrated oxide systems is extremely important to help our understanding of the physics even if these materials, because of crystallinity, may turn out to be unsuitable for technological purposes. In the following we will concentrate on various $M_xL_yO_z$ compounds.
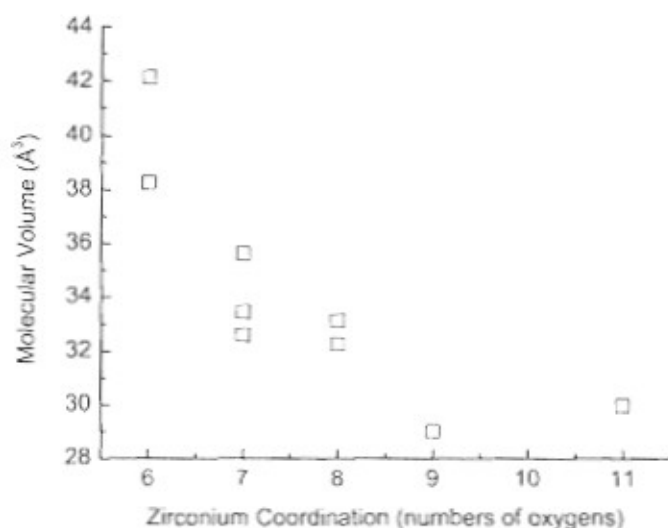
Figure 3. Variation of the molecular volume as a function of Zr coordination in ZrO_2 polymorphs (from reference 18).

3.2.1 *LaAlO₃*

The dielectric constant of crystalline $LaAlO_3$ is ~ 28 and this material would therefore appear to be an excellent candidate for applications as a replacement for SiO_2 as a gate oxide. However, efforts to produce amorphous $LaAlO_3$ have failed to yield films[19] with k > 13 despite earlier reports to the contrary[20]. Detailed investigation of the reasons for this "discrepancy" have revealed that the density of typical amorphous films is approximately 64% of the value of the crystalline phase. This alone is sufficient to justify a substantial reduction in the dielectric constant as is indeed observed. There is presently no atomic distribution data such as extended X ray absorption fine structure which can be

used to probe coordination, etc. However, it is worthwhile noting that in the case of SiO_2, amorphous SiO_2 has a density of 2.2 g cm^{-3} whilst the crystalline phase, quartz, has a density of 2.65 g cm^{-3} indicating that the amorphous phase density is 83% of the crystalline value. In the case of SiO_2 there is no coordination change so these numbers clearly indicate that substantial density differences may also occur between the amorphous and crystalline phases without the need to invoke coordination effects – simply the atoms are less densely packed in the network.
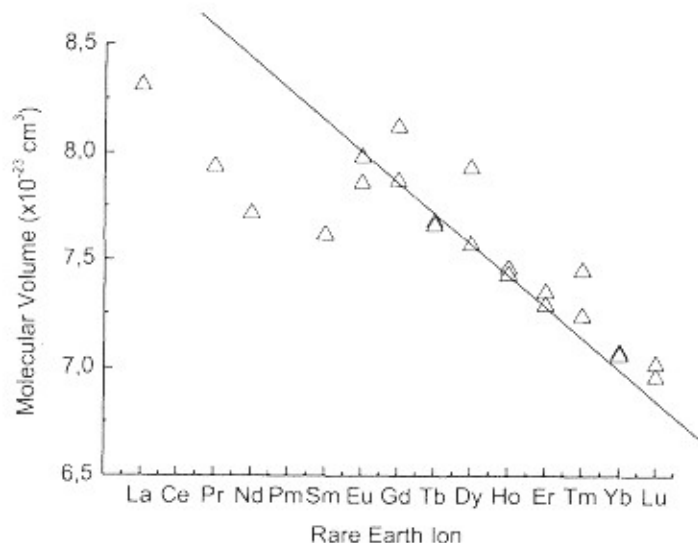

Figure 4. Variation of the molecular volumes as a function of ion in the rare-earth sesquioxide series of compounds. Different values for the same ion correspond to different density values available in the published literature.

3.2.2   Rare-earth sesquioxides

A significant effort has been made to study the dielectric properties of the rare-earth (RE) sequioxide insulators (RE$_2$O$_3$). Technologically, there materials are problematical because they are hygroscopic and react with Si at relatively low temperatures[21]. In general the dielectric constant measured[12] for the heavy RE sesquioxides (atomic numbers $\geq$ Gd) is ~ 12-13. The structure of these

materials is cubic. Though there have been relatively few measurements of the dielectric constants of the lighter RE sesquioxides, values do exist for La, Ce and Pr indicating substantially larger constants in the range 20-31. Why would this be the case ?

In Fig.(4) we plot the molecular volume for the RE sesquioxides as a function of RE ion. One observes that for the lighter RE ions there is a decrease in molecular volume and this is associated with the fact that the lighter RE sesquioxides form with a hexagonal structure[22]. It can therefore be anticipated that the dielectric constants of the lighter RE_2O_3 compounds will be larger than those of the heavier RE_2O_3's because the molecular volumes are smaller. We have ignored potential variations in the molecular polarizabilities and we have no independent means to determine such variations. However, one can reasonably expect that any variation in the polarizability be monotonic across the RE series. Using the dielectric data and the molecular volumes determined in Fig.(4) we plot, in Fig.(5) the anticipated variation of the low frequency polarizability, α. The predicted values of α do, indeed, vary monotonically. We include in Fig.(5) data obtained from a similar analysis on RE garnets $(RE_3Ga_5O_{12})$ where there are no phase changes in the crystalline structure. The variation of α is again monotonic and similar, though different in absolute size, to that anticipated in the RE_2O_3 series but where a phase change does exist. This data gives further credence to the assumption that the significant difference in the dielectric constants of the heavy and light RE_2O_3 compounds is primarily related to the structure of the network.

3.2.3 Ta_2O_5-TiO_2

Tantalum pentoxide has been identified as a technologically useful dielectric in DRAM cell applications but not for applications as a gate oxide replacement in MOSFETs. The reason for the latter is the rather small insulator conduction band-Si conduction band offset (< 1 eV) which could lead to substantial charge injection from the Si substrate into the dielectric. In the amorphous phase the dielectric constant is found to be[23] ~ 25 whilst in the crystalline (orthorhombic) state it is[24-26] 30-50 and 55-64 in the hexagonal phase[27]. One again suspects the presence of effects of molecular volume therefore.

An interesting, and important, effect is detected when Ta_2O_5 is diluted with TiO_2. For a concentration of approximately 8 atomic % TiO_2 in Ta_2O_5 extremely large dielectric constants of ~ 126-189 are observed. Intuitively, one
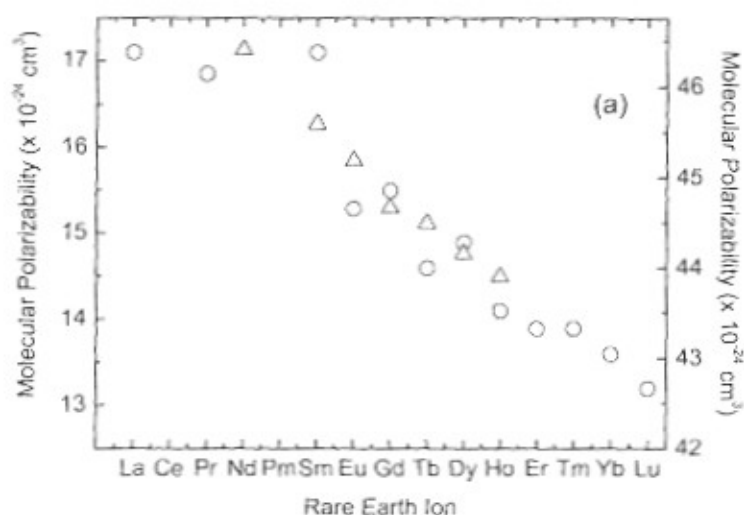
Figure 5. Variation of the molecular polarizability in (O) RE_2O_3 compounds (left hand scale) and (△) $RE_3Ga_5O_{12}$ compounds (right hand scale) as deduced from experimental densities and dielectric constants.

might anticipate that this dramatic increase is in some way related to the large dielectric constant (~ 100) of crystalline TiO_2. However, the mixed oxide contains only 8 atomic % of this material. It turns out that the addition of small quantities of TiO_2 to Ta_2O_5 stabilizes a dense, monoclinic structure of Ta_2O_5 and we can therefore anticipate the presence of network density related dielectric enhancement. In Fig.(6) we plot the measured dielectric constants for the various phases of Ta_2O_5 as a function of the inverse of α/V_m. For the sake of discussion we have assumes $\alpha \sim 20.2 \times 10^{-24}$ cm^3. Also shown in the plot is the theoretical curve generated using Eq.(3). Inasmuch as we have maintained a constant, the entire variation of the dielectric constant is attributed to the

density differences of the different Ta_2O_5 polymorphs. Some minor variation in α may occur as a function of density but as we have shown in the examples given previously, their overall variation does not mask the primary variable which is the network density.
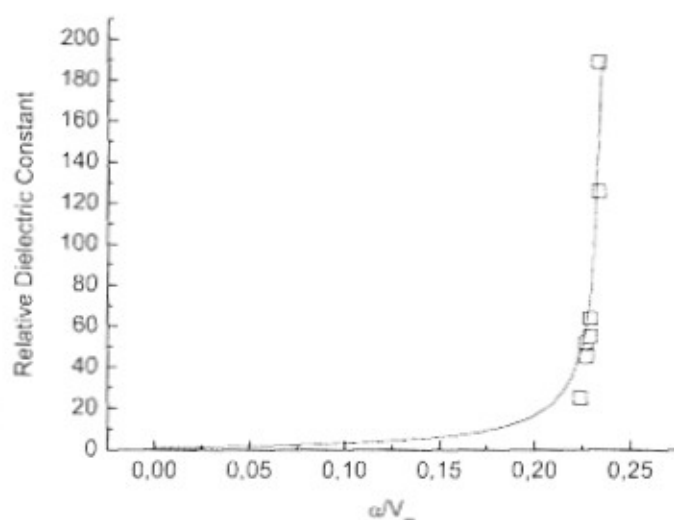

Figure 6. Relative dielectric constant in Ta_2O_5 polymorphs as a function of α/V_m with α taken as 20.2×10^{-24} cm^3. The solid line shows the predicted variation from Eq.(3).

4. CONCLUSIONS

In this paper we have reviewed the role of the network in determining the dielectric constant of binary and mixed oxides. We have discussed what were seemingly difficult and misunderstood systems such as Ta_2O_5-TiO_2 which appeared to have an anomalously large dielectric constant. Furthermore, we have been able to explain seemingly controversial data on RE sesquioxides which appeared to demonstrate very much larger dielectric constants for the

lighter RE's than for the heavy RE's. The conclusion we draw is that network volume and connectivity plays a crucial role in determining k.

- On the basis of the analysis presented here it appears that the dielectric constant of the amorphous phase of any binary or mixed oxide will always be significantly lower than that for the crystalline phase. This appears to result from the fact that the amorphous network is less densely packed than the crystalline phase.
- The role of coordination is extremely important since higher coordination structures result in denser networks. This may be true in both amorphous and crystalline phases. The data on ZrO_2 polymorphs demonstrates the density/coordination perfectly for the crystalline state.
- Some crystalline phases which are not normally stable may become so by addition of stabilizing components (such as TiO_2 in Ta_2O_5). Denser structures and associated higher k values may be obtainable by this route.

These arguments neglect the possible variation of molecular polarizability which, if large enough and of the correct sign, could negate the effects of reduced molecular volume resulting in denser structures. Fortunately, all of the systems we have studied to data appear to indicate that the volume diminution effect dominates.

For technological applications, high k amorphous materials are generally supposed to be the material most desired since possible effects due to grain boundaries are absent. The present work leads us, unfortunately, to the natural conclusion that the amorphous state is the most unsuitable if we want to obtain the maximum k values. At the present time there appears to be no obvious solution to this dilemma.

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